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Preliminary investigation of high-*k* materials –TiO_2 doped Ta_2O_5 Films by remote plasma ALD

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Abstract

$(TiO_2)_x(Ta_2O_5)_{1-x}$ (x is up to 0.45) films deposited by a remote plasma atomic layer deposition (ALD) are reported in this work. The growth rates of the ALD films measured by ellipsometer are in a range of 0.8 - 1.06 Å/cycle at a deposition temperature of 300°C, depending on Ti/(Ti+Ta) ratio. In order to evaluate the high-*k* materials of Ti-doped Ta_2O_5 films, EDX and AES were used for determining the composition of the films. The thickness and optical properties of the films were measured by a spectral ellipsometer and CV-measurement was applied for testing the electrical property of the film. Furthermore, the effects of thermal annealing and in-situ O_2-oxidation on thickness, refractive index and electrical property of $(TiO_2)_x(Ta_2O_5)_{1-x}$ films are also discussed.PACS: 82.47.Tp

Key words: *electron-emitter; surface conduct; W-Si-N thin film; nanocrystal structure*

Introduction

Driven by the shrinking of microelectronic devices there is a strong demand for novel ultra high-*k* dielectrics (UHK) and electrode materials. When a new functionality on a chip can be created by simply adding a few process modules above the baseline CMOS flow (as well as DRAM and e-DRAM), this will almost always be preferred from a cost perspective over a heterogeneous integration approach. The integration of passive devices on a chip (e.g. capacitors) has been plagued with a scaling problem. Much larger capacitance densities are required. This can only be achieved by switching to ultra high-k materials in combination with noble metal or conductive metal oxide electrodes.

Ultra high-dielectric constant thin films such as $(TiO_2)_x(Ta_2O_5)_{1-x}$ ($TiTaO_y$), $SrTiO_3$ (STO) and (Ba,Sr) TiO_3 (BSTO) [1-5] have attracted great interest as the capacitor dielectrics of dynamic random access memory (DRAM) devices. It has been reported that the dielectric constant of $(TiO_2)_x(Ta_2O_5)_{1-x}$ bulk materials (x=0.08) is over 120 [1]. Compared to pure Ta_2O_5 thin films, significant enhancement in dielectric constant is obtained by adding small

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quantity of TiO_2. It is a general agreement that the dielectric permittivity of Ta_2O_5 is 20-25. However, the mechanism of enhanced the dielectric permittivity of the TiO_2 doped Ta_2O_5 played as an UHK material, are not understood clearly. In general, the appearance of high-temperature phase (H-Ta_2O_5) has been observed [1]. It seemed that the enhanced dielectric permittivity might be associated with the appearance of H- Ta_2O_5. There are two ways to form a high-temperature phase and stabilise it to room temperature: Rapid Thermal Processing (***RTP***) in a high temperature/energy and adding small quantities of additives such as TiO_2. [1, 6] However, the low-temperature phase of Ta_2O_5 (L-Ta_2O_5) transforms to the high-temperature phase (H-Ta_2O_5) at about 1360°C, while it undergoes several phase transitions on cooling from high temperature [7–9]. Thus, it is difficult for conventional furnace sintering to achieve an appropriate H- Ta_2O_5 phase at room temperature. Therefore the approach of adding small quantities of additives into Ta_2O_5 is a common way to enhance its dielectric permittivity.

There are many techniques to have been used for deposition of these UHK films. Gan and co-authors reported that the dielectric constant of $(TiO_2)_x$-$(Ta_2O_5)_{1-x}$ thin films prepared using radio-frequency magnetron sputtering deposition appears to critically depend on the amount of TiO_2 incorporated into the film and post-anneal condition. The highest value of dielectric constant is about 55 for a TiO_2 content of 8% and annealing at 800 °C [10]. Kaliwoh the maximum values of dielectric constant of $(TiO_2)_x$-$(Ta_2O_5)_{1-x}$ thin films, deposited by UV-photon enhanced CVD, were also recorded at TiO_2 content of 8% [11]. The low-temperatures, (<500°C) metallorganic chemical vapor deposition (MOCVD) process has been studied for producing the UHK thin films for DRAM applications [12, 13]. However, no conformal deposition over the entire surface area of such an extreme geometry in terms of the chemical composition as well as the thickness has been confirmed used above mentioned approaches even for low temperature MOCVD processes. [2, 12, 13]

Recently, atomic layer deposition (ALD) technology is widely used for both of materials researches and coating extreme geometries of devices, due to its self-limiting growth model, composition accurately controlling and conformal deposition even for high aspect ratio [14,15]. ALD is able to meet the both needs for atomic layer control and conformal deposition using sequential, self-limiting surface reactions. However, there is little publication on ALD $TiTaO_x$ to be found, to the best of our knowledge. In this paper, $(TiO_2)_x(Ta_2O_5)_{1-x}$ films growth by O_2-plasma ALD at temperatures as low as 300°C were carried out. In particular, the effects of Ti/Ta ratio on film deposition characteristics such as the growth rate, refractive index, bond gap and dielectric constant are reported. Furthermore, the effect of thermal anneal and in-situ O_2-oxidation of the as-deposited films on thickness, refractive index and electrical property of $(TiO_2)_x(Ta_2O_5)_{1-x}$ films are also discussed.

Experimental

An Oxford Instruments FlexAL® ALD reactor, which can performance both of remote plasma ALD and thermal ALD capabilities within a single system, was used for this work. Figure 1 shows schematic of the FlexAL® reactor. The process of $(TiO_2)_x(Ta_2O_5)_{1-x}$ (x is up to 0.45) films carried out by the remote O_2-plasma ALD at 300°C, using tbutylimido tris(dimethylamido) tantalum (TBTMET) and titanium isopropoxide (TIIP) as Ta and Ti source, respectively. TTIP and TBTMET were vaporized at 45°C and 55°C, respectively, using the normal bubbling method with 200sccm of Ar gas flow as the carrier and purge gases. A laminate structure of $(TiO_2)_x(Ta_2O_5)_{1-x}$ was deposited that includes both sub-loops for TiO_2 and Ta_2O_5 ALD growth, the sub-loop numbers depend on Ti/(Ti+Ta) ratio. ALD chamber pressure was varied from 15 to 80 millitorr during the process steps. Not only the wafer holder stage was heated but also the chamber wall and delivery line were heated to a temperature of 150°C and 70°C, respectively, to prevent the precursor condensation and make the sample surface temperature the same. The remote O_2 plasma was generated by a radio frequency (rf) induction-type plasma generator (ICP). The plasma power was 300 W.

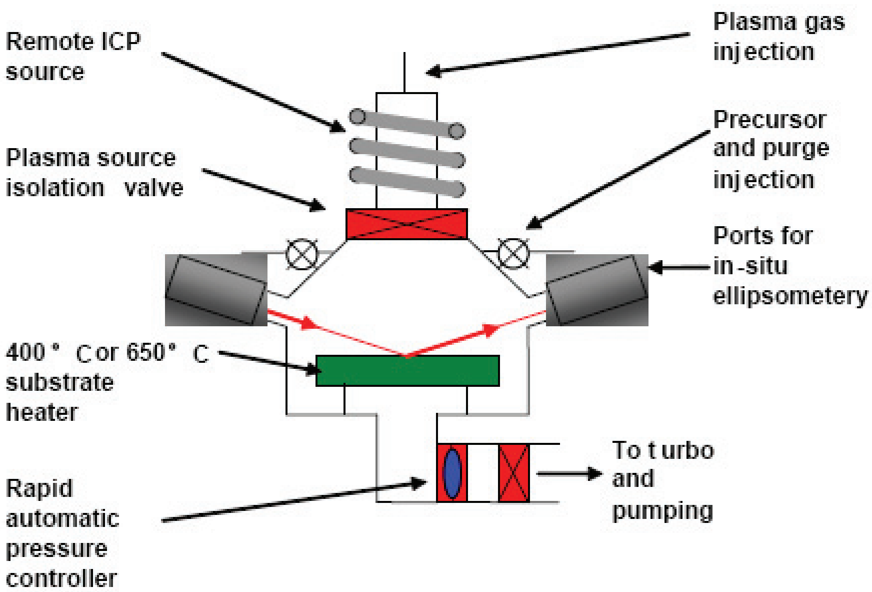

Figure 1, schematic of the FlexAL® reactor.

The thickness and the refractive index of the ALD films were measured using a J.A. Woollam M2000V spectroscopic ellipsometer (370nm-1000nm wavelengths). An ex situ phase modulated spectroscopy ellipsometer (Model UVISEL JOBIN-YVON) in the spectral range of 0.75-6.5 eV with a step of 0.05 eV at an incident angle of 70 ° was used to determined the optical properties of the $TiTaO_y$ samples of various Ti/Ta ratios and at different substrate temperatures. Energy dispersive X-ray (***EDX***) (Oxford Instruments) and Auger Electron Spectroscopy (***AES***) were used for determining the chemical composition and element profile of the films. CV-measurement was applied for testing the electrical property of the film. In order to investigate the effect of annealing on the electrical, optical and micro-structural properties of the films, two anneal processes were carried out: 1) thermal anneal in air from 400°C to 700°C for 30 min and 2) in-situ O_2-oxidation at same deposition temperature of 300°C for from 0.5 min to 4 min.

Results and discussion

ALD films growth

TiO_2 doped Ta_2O_5 ($TiTaO_x$) films were deposited on Si with TiO_2 mol% up to 45%. Figure 2 shows the growth rate and refractive index of $(TiO_2)_x(Ta_2O_5)_{1-x}$ laminate films with TiO_2-composition in the films. The growth rate (GR) decreases with increasing TiO_2 ratio, while refractive index (RI) increases with increasing TiO_2 ratio at 300°C. The GR of the ALD films is in a range of 0.8 - 1.06 Å/cycle and RI is in a range of 2.08 - 2.19, depending on Ti/(Ti+Ta) ratio. It is noted that the relationships of GR and RI with TiO_2-ratio are not linear in the range of 7%-12%, which implied that there are some micro-structural changing in the laminate material, which lead to these turning points of optical property and growth rate.

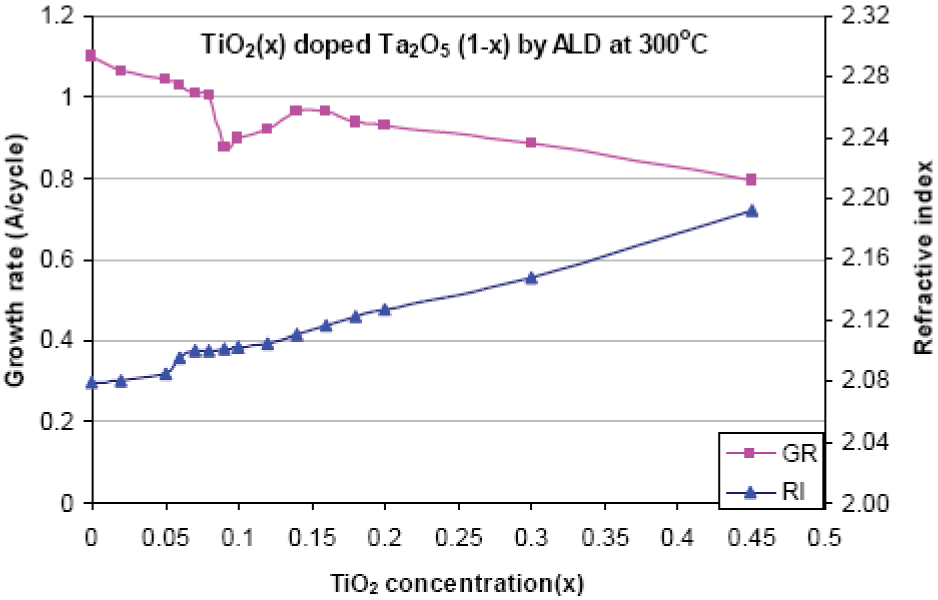

Figure 2, growth rate & refractive index of TiTaOx vs TiO2-composition in the films

Ta_2O_5 films were deposited by using TBTMET and O_2 plasma to compare their growth rates and optical constants with $(TiO_2)_x(Ta_2O_5)_{1-x}$ laminate films. The results show the growth rate (GR) of pure Ta_2O_5 at 300°C is around 1.10 Å/cycle and refractive index (RI) of the films is 2.150 (not show here).

Figure 3 shows the AES of a Ta_2O_5 ALD film with thickness of 33nm on Si/SiO_2, Ta : O $\approx$ 1 : 2.5 , no carbon in bulk was found and detected only on the surface. Figure 4 is AES profile graph of an 8%TiO_2 doped Ta_2O_5 on a substrate of Si/ native SiO_2. No carbon in bulk was found and the inset of the graph shows interface native SiO_2 of the substrate.

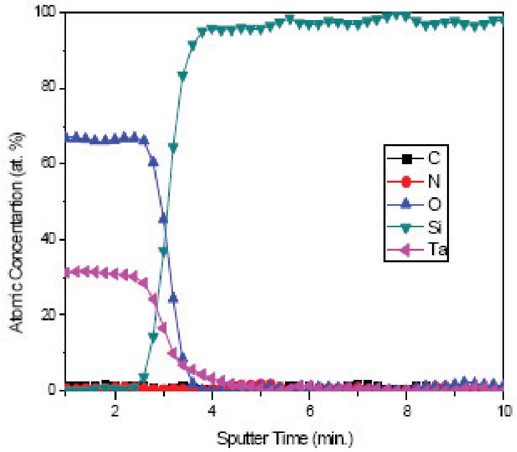

Figure 3, AES of Ta_2O_5 by plasma-ALD.

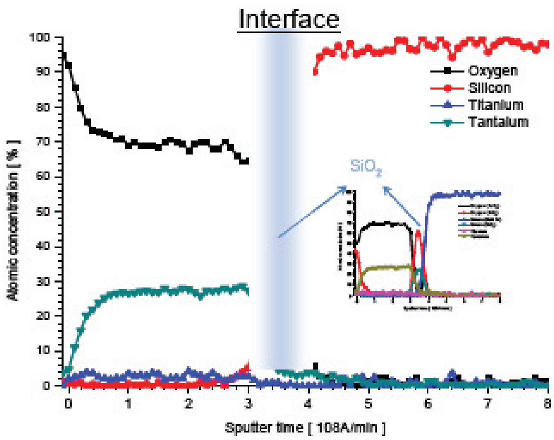

Figure 4, AES of $(TiO_2)_x(Ta_2O_5)_{1-x}$ (x=0.08) by plasma-ALD

In-situ oxidation and Thermal annealing

To investigate the effect of annealing on material properties, TiO_2 doped Ta_2O_5 ($TiTaO_y$) films were applied for both in-situ O_2-plasma oxidation and thermal annealing (in air for 30min). The results show in Figure 5 and Figure 6:

1) **In-situ oxidation**

Fig.5 shows that thickness of $TiTaO_y$ film reduced fast in in-situ oxidation at the first minute then it goes flat, while refractive index of $TiTaO_y$ increases with O_2-plasma oxidation time. This result tells that there are some optical and micro-structural changes in the film during a short-time of in-situ oxidation.

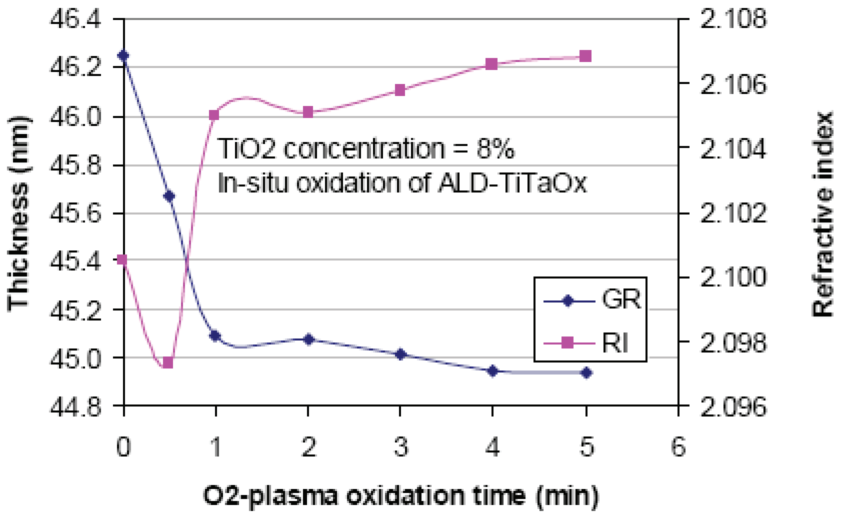

Figure-5, thickness & RI changing of TiO2 doped Ta2O5 (x=8%) films vs in-situ O_2-plasma oxidation time at 300°C.

2) **Thermal annealing**

Fig.6 shows that thickness of $TiTaO_y$ film reduced with anneal temperature, there is a turning point change starting at 450°C.

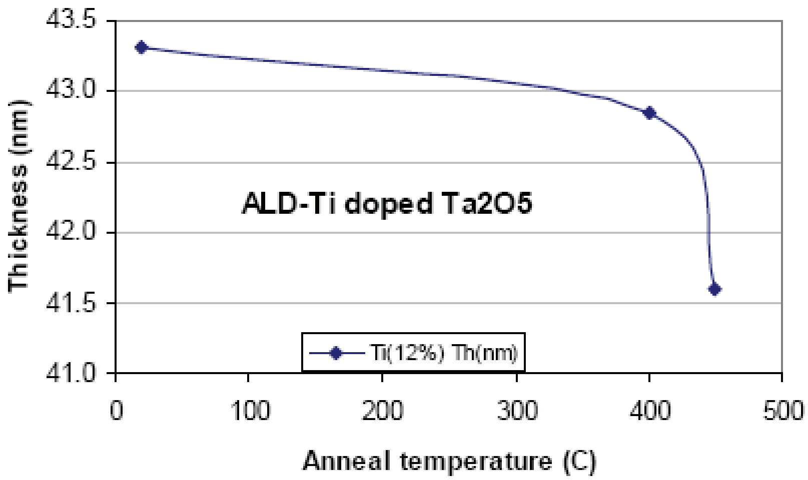

Figure-6, thickness changing of TiO_2 doped Ta_2O_5 (x=12%) films vs thermal annealing time (in air for 30min).

Both in-situ oxidation and thermal annealing processes can increase the density (reducing thickness), and refractive index of the films. In-situ O_2-plasma oxidation is comparable with thermal annealing, but it needs only very short time and within the deposition step.

Optical properties by spectroscopic ellipsometry

In order to investigate the effects of doping TiO_2 into Ta_2O_5 on optical constants and optical properties of ALD $(TiO_2)_x(Ta_2O_5)_{1-x}$ thin films, spectroscopic ellipsometry (SE) was applied to characterize a series of the samples. A simple optical model consisting of a three-layer stack structure: Si/$TiTaO_y$/ambient was used for the analysis. The unknown optical constants and pseudodielectric functions of $TiTaO_y$ thin films were constructed using a modified classical dispersion model relation in the following form:

$$(n+ik)^2 = \varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)\omega_t^2}{\omega_t^2 - \omega^2 + i\Gamma_0\omega} \qquad (1)$$

During the simulation, the films thickness and the dispersion coefficients were fitted through χ^2 (goodness of fit [16]) minimization process. And at last, the film thickness and the pseudodielectric functions $< \varepsilon = \varepsilon_1 + i\,\varepsilon_2 >$ were extracted based on the best fit between the experimental SE data and the simulated spectra.

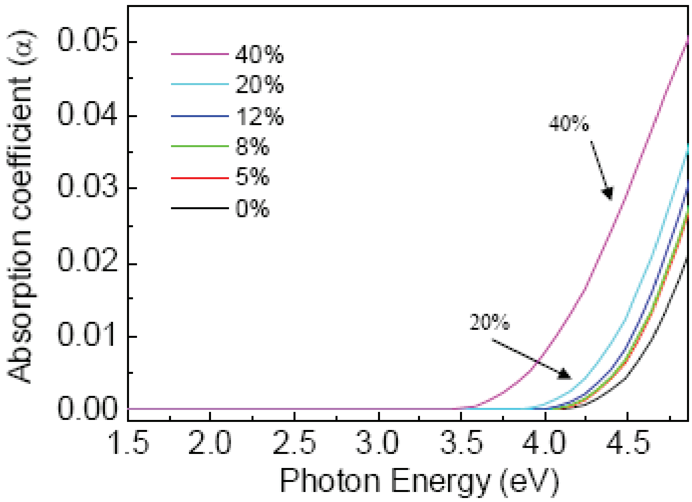

Figure 7, the absorption coefficient of the TiTaOy films with different Ti-incorporation content.

In order to discuss the optical properties, the absorption coefficients (α) were calculated using $\alpha=4\pi\kappa/\lambda$, where λ was the wavelength of a photon and κ was the corresponding extinction coefficient extracted based on SE fitting results. Figure 7 gives the results of the absorption coefficients of the TiTaOy films with different Ti-incorporation content. Since ALD $(TiO_2)_x(Ta_2O_5)_{1-x}$ system has an indirect fundamental gap, the interband absorption can be expressed by the following equation [17]:

$$\alpha h\upsilon \propto \left(h\upsilon - E_g\right)^2 \qquad (2)$$

Where E_g is optical band gap energy. By plotting the $(\alpha h\nu)^{1/2}$ vs photon energy (hν) curves near the band edge for all the samples (shown in figure 8), E_g values are estimated. It is expected that absorption coefficients (α) decreases with adding doped TiO_2 into Ta_2O_5 due to TiO_2 with band-gap of 3.03 eV for rutile and 3.18 for anatase.

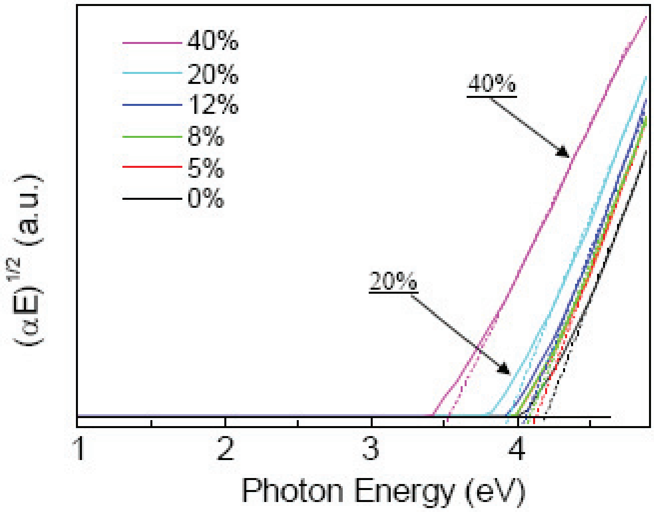

Figure 8, the optical band gap which is determined by the energy dependence characteristic of the indirect allowed transition as illustrated by the (αhv)1/2 vs the photon energy (hv).

Table 1 shows the optical band gap of ALD- TiO_2 doped Ta_2O_5 films as-deposited and after thermal annealing. It is obvious that the optical band gap (E_g) shows a blue shift after the additional annealing only up to 550^{o}C. According to Pauling's theory [18], the increased E_g value is due to the increased stoichiometric in oxide films because of the oxidization of sub-oxidized $TiTaO_y$ in air ambient at high temperature.

Table-1 Optical band gap of ALD- TiO_2 doped Ta_2O_5 films As-deposited and after thermal annealing

Ti content (atom%)	Annealing temp (ºC)	Thickness (nm)	Eg (eV)
0	0	46.416	4.038
	400	45.627	4.047
	550	44.860	4.057
5	0	50.317	3.985
8	0	47.740	3.983
	400	47.700	3.983
	550	46.293	3.988
12	0	43.308	3.933
	400	41.601	3.939
	550	42.841	3.945
20	0	44.122	3.802
40	0	35.11	3.412
	400	35.07	3.434
	550	34.38	3.457

Electrical properties

Table 2 shows a summary of electrical and physical properties of $(TiO_2)_x(Ta_2O_5)_{1-x}$ layers by plasma-ALD.

The sample name starting with "A" means as-deposited films and with "P" means the samples are treated by in-situ oxidation at 300°C or thermal annealing at a temperature of 700°C. From the data in the table we can find it is very clear:

(1) Both in-situ oxidation or thermal annealing can increase film density (reduce film thickness) and refractive index of of $(TiO_2)_x(Ta_2O_5)_{1-x}$ films.

(2) Both treatments of the films can increase the film capacitance and dielectric constant.

(3) In-situ O_2-plasma oxidation of the $(TiO_2)_x(Ta_2O_5)_{1-x}$ films at 300°C for 4min is comparable with that of thermal annealing at 700°C for 30min.

(4) The highest dielectric constant measured of 27 at 1MHZ (39 at 100HZ) in these ALD TiTaOy films does not improve them too much, which shows the laminate structure by ALD is not good enough for the integration of both Ti and Ta composites.

Table-2

Electrical and physical properties of TiO_2-dope Ta_2O_5
(sample-A) as-deposited by plasma ALD
(sample-P) after annealing by in-situ oxidation and thermal annealing.

Samples	TiO_2 (x %)	Annealing	Thickness (nm)	Refractive index	Capacitance (pF) @1MHz	Capacitance (pF) @100Hz	Dielectric constant k @ 1MHz	Dielectric constant k @ 100Hz
A-03	5	As-deposited	45.74	2.0949	183	224	20	22
P-03	5	In-situ oxidation (4min)	45.04	2.1018	231	305	21	25
A-06	8	As-deposited	40.69	2.1014	228	275	21	23
P-06	8	In-situ oxidation (4min)	40.17	2.2062	250	351	27	35
A-08	12	As-deposited	40.92	2.1055	202	251	20	22
P-08	12	In-situ oxidation (4min)	40.14	2.1106	261	298	26	39
A-07	10	As-deposited	42.01	2.1044	210	252	20	23
P-07	10	Thermal anneal (700Cfor 30min)	41.48	2.1143	223	277	23	30

As well known, most of the as-deposited ALD oxides are amorphous. It understood that dielectric permittivity of crystalline is higher than that of amorphous structure. The formation of H- Ta_2O_5 phase in the $(TiO_2)_x(Ta_2O_5)_{1-x}$ films might be a key point to enhance their dielectric permittivity. The laminate structure by ALD, however, is added a single layer of TiO_2 into multilayer Ta_2O_5. The films are, basically, chemical component is not uniform. It requires further works to investigate a uniform diffusion of TiO_2.into Ta_2O_5 films and form H- Ta_2O_5 phase by annealing.

Another possible approach is the co-deposition of TiO_2.and Ta_2O_5 by ALD and associates with an improved annealing process for the films to increase the dielectric constant of the $(TiO_2)_x(Ta_2O_5)_{1-x}$.

Conclusions

Uniform and composition accurately controlled $(TiO_2)_x(Ta_2O_5)_{1-x}$ laminate films have been deposited on Si substrates by using remote plasma ALD technology. The growth-rate of the ALD films are in a range of 0.8 - 1.06 Å/cycle at 300°C, depending on Ti/(Ti+Ta) ratio.

AES profile measurements of TiO_2 doped Ta_2O_5 show the composition of the films can be well control and no carbon is in bulk of the film. Both in-situ oxidation and thermal annealing processes can increase the density, refractive index, capacitance, and dielectric constant of the films. In-situ O_2-plasma oxidation is comparable with thermal annealing up to 700^{o}C, the advantages are that it needs only a short time and integrates within the ALD deposition step.

This preliminary investigation of TiO_2 doped Ta_2O_5 Films shows the laminate structure by ALD is not good integration of both Ti and Ta composites. Co-deposition of the high-k materials by ALD and improved annealing process for the films are planed in the next approach to increase the dielectric constant of the $(TiO_2)_x(Ta_2O_5)_{1-x}$.

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